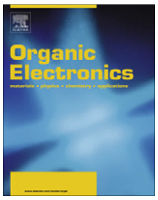
Organic Electronics 14 (2013) 236–249

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Flexible organic light-emitting diodes on a polyestersulfone (PES) substrate using Al-doped ZnO anode grown by dual-plasma-enhanced metalorganic deposition system

Po-Hsun Lei [*], Chia-Ming Hsu, Yu-Siang Fan

Institute of Electro-Optical and Material Science, National Formosa University, No. 64, Wunhua Rd., Huwei, Yunlin County 632, Taiwan

ARTICLE INFO

Article history:
Received 26 June 2012
Received in revised form 2 October 2012
Accepted 13 October 2012
Available online 23 November 2012

Keywords:
Al-doped ZnO (AZO)
Dual-plasma-enhanced metalorganic chemical vapor deposition (DPEMOCVD)
Organic light-emitting diodes (OLEDs)
Polyestersulfone (PES)

ABSTRACT

This study proposes flexible organic light-emitting diodes (OLEDs) grown on polyestersulfone (PES) using Al-doped zinc oxide (AZO) as the anode, fabricated by the dual-plasma-enhanced chemical vapor deposition (DPEMOCVD) system. The experimental results including crystalline structure, optical, and electrical characteristics indicate that the quality of AZO films grown on PES depends on the deposition temperature and Al content. The optimal deposition temperature and Al content for AZO film are 185 °C and 2.88 at%, respectively. Further increasing or decreasing the deposition temperature and Al content degrades the quality of AZO films. The optimal AZO film deposited on the PES substrate was used as the anode for flexible OLED. It shows a similar performance compared to OLEDs using commercial indium–tin-oxide (ITO) as the anode on glass, and represents enhanced characteristics to that of the commercial ITO anode on a flexible polyethylene naphthalate (PEN) substrate. This indicates that the DPEMOCVD-deposited AZO film on the PES substrate can be the anode for flexible OLEDs.

1. Introduction

Transparent conductive oxide (TCO) has been extensively investigated because it is one of the most important components in building electronic, optoelectronic, electrochemical, and electromechanical devices, such as organic or inorganic light-emitting diodes [1–3], solar cells [4,5], transistors [6], and electrodes for liquid crystal display (LCD). Among these applications, organic light-emitting diodes (OLEDs) based on small molecules are considered promising candidates for large-area full-color flat-panel display and solid-state lighting because of their potential low cost and high efficiency. Indium–tin-oxide (ITO) has previously been the most commonly used anode material for OLED in display and lighting applications because of its high transparency over visible range, low resistivity, and relatively high work function [7,8]. However, indium is chemically unstable in reducing ambience, and its limited resource may cause problems to satisfy future demand. In addition, ITO used in OLED has several disadvantages including the rare, and thus, high cost of indium, a high-energy barrier for hole injection at the interface of the hole transport layer, chemical instability in reducing ambience, indium diffusion into organic layers, and spikes or asperities in the ITO film [9–11]. To improve the negative characteristics of ITO applied to the OLED, numerous metal oxides have been actively investigated as an alternative to TCO films. Among these metal oxides, zinc oxide (ZnO) is a natural selection over In-rich ITO because of its high conductivity, good optical transmittance, high thermal stability, abundance, and low-cost fabrication [12–14]. Because of natural defects, undoped ZnO is an n-type semiconductor. To reduce conductivity and high transmittance in the visible range, ZnO can dope group III elements such as aluminum (Al) [15], gallium (Ga) [16], indium (In) [17], and boron (B) [18]. Doped ZnO has similar optical and electrical properties to ITO. Among these doped-ZnO films,

---

[*] Corresponding author.
E-mail address: pohsunlei@gmail.com (P.-H. Lei).

1566-1199/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.orgel.2012.10.030

Al-doped ZnO (AZO) is a particularly attractive material because of low cost, good resistance against damage by hydrogen plasma, abundance, and thermal stability.

TCOs coated on a glass substrate are the most commonly selected substrate for OLEDs. However, glass is limited by its intrinsic inflexibility, thickness, and weight characteristics for the demands of future OLED development in displays and lighting. OLEDs grown on flexible TCO substrates used as flexible electrodes have recently gained considerable attention because of the advantages of low cost, light weight, robust profile, roll and fold for portability, and the ability to construct a device with any geometry and shape [19,20]. To fabricate high-performance flexible OLEDs, several plastic materials such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polypropylene adipate (PPA), polycarbonate (PC), and polyestersulfone (PES) [21–25] are promising flexible substrates with a flexible transparent conducting oxide (TCO) as the anode electrode to effective hole-carrier injection into the organic layer. Among these flexible substrates, PES has several superior characteristics including excellent thermal stability, high optical transmittance over a visible range, better electrical insulation, light weight, high flexibility, low water absorption, and low optical loss. These properties make it one of the most promising substrates for a flexible OLED substrate.

To avoid flexible substrate degradation, methods or technologies with low growth temperature and energetic particle bombardment, such as sputtering [21], pulsed laser deposition (PLD) [26], atomic layer deposition (ALD) [27], and plasma-enhanced metalorganic chemical vapor deposition (PEMOCVD) [28], have been applied to fabricate AZO thin films on flexible substrates. Excellent AZO films with preferential (0 0 2) orientation can be achieved through sputtering, PLD, and ALD technologies; however, these technologies are inadequate for high throughput and large-area OLED displays because of the low growth rate. The PEMOCVD system demonstrates numerous key advantages, including high growth rate, large area uniformity, low growth temperature, conformity, and easy integration within the preparation scheme of a complete device. Low-temperature-grown AZO films with superior electrical and optical characteristics can be deposited on hard substrates by appropriate plasma power; however, reports on AZO films grown on flexible substrates are rare. Substrate heating caused by energetic ion bombardment in high-density plasma can also result in deformation of the flexible substrate. Researchers have recently reported that the remote-plasma chemical vapor deposition (RPCVD) method can alleviate ion bombardment by placing the plasma system away from the substrate [29]. However, the free radicals of oxidizing agents might vanish or return to molecules during diffusion to the substrate surface. This study presents flexible AZO grown on PES using a modified PEMOCVD system with two plasma systems, including an RF plasma system and a DC plasma system, to reduce ion bombardment effect, low dissociation of oxygen (O_2), and growth temperature [30]. The electrodes of a RF plasma system are parallel to the normal substrate in a DPEMOCVD system to alleviate the ion bombardment effect. The DC plasma system is used to enhance the dissociation of O_2. A high vacuum environment is built into the DPEMOCVD system to increase the mean free path of oxygen free radicals (O^*). In addition, the deposition temperature is significant to AZO thin films grown on PES. To avoid deformation of the PES substrate, the deposition temperature is maintained below 200 °C in this study.

2. Experimental details

2.1. Growth of AZO film on flexible PES substrate

A high ionization rate for O_2 is important to react with the DEZn and TMAl completely, allowing a high-quality AZO film with well-controlled stoichiometry to grow on the PES substrate. However, the ionization rate in conventional PECVD systems is low, particularly O_2 with strong bond energy. To enhance the dissociation of O_2 and increase the concentration of oxygen free radicals (O^*), the proposed DPEMOCVD system was used to grow AZO thin film. The DPEMOCVD apparatus includes dual plasma systems with a DC voltage driven and an RF plasma system, gas delivery system, heating system, and vacuum system. In this dual plasma system, oxygen free radicals ionized by the DC voltage driven plasma system diffuse to the substrate, which is surrounded by an RF plasma system to reduce the recombination of oxygen free radicals during the growth process. Unlike a conventional PEMOCVD system, the RF plasma system electrodes are parallel to the substrate surface normal. An automatic-matched network controls the RF power coupled to the chamber to maintain constant power. The Al content in AZO thin films was controlled by the TMAl flow rate from 15 to 24 sccm. The deposition parameters for AZO films grown by DPEMOCVD are listed in Table 1. The crystalline structure of the AZO thin film was characterized by X-ray diffraction (XRD) patterns using a Bruker D8 advanced diffractometer equipped with a Cu Kα (λ = 0.154 nm). The surface morphology of AZO thin films on PES was measured using an atomic force microscope (AFM; D13100, Digital instruments Veeco Metrology Group). The transmittance of AZO thin films in the visual range was measured using a UV–Vis–NIR spectrophotometer (UVD-350). The electrical properties, including carrier concentration, carrier mobility, and resistivity, were measured by Hall measurements (HMS-5000) at room temperature. The thickness of the AZO films grown on the PES substrate for crystalline, optic, and electrical measurement were maintained at 2500 nm.

Table 1
Deposition parameters for DPEMOCVD-AZO film.

Chamber pressure (Pa)	2.25E-4
Deposition temperature (°C)	160–190
Thickness of ZnO	2500 A
RF power	350 W
DC power	1.8 W
DEZn flow rate (sccm)	15
O_2 flow rate (sccm)	180
TMA flow rate (sccm)	18